

Continuous magnetic phase transition in half-frustrated $\text{Ca}_2\text{Os}_2\text{O}_7$

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We present the specific heat, magnetization, optical spectroscopy measurements and the first-principle calculations on the Weberite structure $\text{Ca}_2\text{Os}_2\text{O}_7$ single crystal/polycrystalline sample. The $\text{Ca}_2\text{Os}_2\text{O}_7$ shows a Curie-Weiss nature at high temperature and goes into a ferrimagnetic insulating state at 327 K on cooling. A λ -like peak is observed at 327 K in the specific heat implying a second-order phase transition. The vanishing electronic specific heat at low temperature suggests a full energy gap. At high temperature above the transition, small amount of itinerant carriers with short life time τ are observed, which is gapped at 20 K with a direct gap of 0.24 eV. Our first principle calculations indicate that the anti-ferromagnetic (AFM) correlation with intermediate Coulomb repulsion U could effectively split Os(4b) t_{2g} bands and push them away from Fermi level(E_F). On the other hand, a non-collinear magnetic interaction is needed to push the Os(4c) bands away from E_F , which could be induced by Os(4c)-Os(4c) frustration. Therefore, AFM correlation, Coulomb repulsion U and non-collinear interaction all play important roles for the insulating ground state in $\text{Ca}_2\text{Os}_2\text{O}_7$.

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I. INTRODUCTION

Metal-insulator transition (MIT) is one of the important phenomena in condensed matter physics and has attracted much attention. Many transition-metal oxides containing partially filled d orbitals, such as NiO, V_2O_3 , have been identified experiencing such transition [1–3]. Early in 1949, Mott and Hubbard proposed that the on-site Coulomb interaction plays an important role in the narrow band materials[4]. Large on-site Coulomb repulsion energy could split the band into two. In general, the correlation effect depends on the value of U/W , where W is the band width, and U is the Coulomb repulsion energy. For 3d transition metal oxides, the band width W is small and the Coulomb repulsion energy (U) is relatively big, which could lead to $U/W \gg 1$. So 3d metal oxides usually belong to strong correlation limit and many of them would be insulating. For 4d/5d metal oxides[5], their band widths W are larger than that of 3d compounds. The larger spatial extent of 4d/5d wave functions also means that the on-site Coulomb repulsion is smaller. Therefore 4d/5d materials are generally less strongly correlated than 3d materials, and lead to $U/W \sim 1$. Simultaneously, as the atomic mass increasing, the spin-orbital coupling (SOC) becomes more and more important, which also play essential role in 4d/5d materials. With these two effects, the electronic properties of 4d/5d metal oxides become more complex and abundant; many new physical phenomena emerge.

Recently, some partially filled 5d transition metal oxides, such as Sr_2IrO_4 [6, 7], $\text{Cd}_2\text{Os}_2\text{O}_7$ [10], $\text{Ca}_2\text{Os}_2\text{O}_7$ [8], $\text{Ca}_3\text{LiOsO}_6$ [9] et al., were found insulating at low temperature, which stimulated many experimental and theoretical studies[6–8, 10, 11]. One novel type of Mott insulating state was observed in the Ir^{+4} based Sr_2IrO_4 [7].

The unusual insulating state is attributed to the cooperative interactions of electron correlation and large spin-orbit coupling[6]. This study is very helpful to the understanding of the MIT in 5d transition metal compounds. On the other hand, for the pyrochlore structure material $\text{Cd}_2\text{Os}_2\text{O}_7$, a continuous metal-insulator transition was observed by resistance, specific heat, magnetization, Hall effect, thermal conductivity and the optical conductivity measurements[10, 11]. In this compound, Os 5d t_{2g} bands are half filled because that the $\text{Cd}_2\text{Os}_2\text{O}_7$ adopts the octahedral environment of OsO_6 with $5d^3$ configuration so that the t_{2g} band is expected near half filling. As we all know, SOC is weak in $S = 3/2$ configuration of the half-filled t_{2g} band for its total orbital angular momentum $L=0$. One more important issue in $\text{Cd}_2\text{Os}_2\text{O}_7$ is that, every Os ion is shared by two Os tetrahedrons, and frustrated with each other. The large nearest neighbor coordination number would cause a wider Os band width[12]. So the mechanism proposed in Sr_2IrO_4 is not suitable for $\text{Cd}_2\text{Os}_2\text{O}_7$. Padilla et al attributed this continuous metal-insulator transition in $\text{Cd}_2\text{Os}_2\text{O}_7$ to a Slater transition[10], which is driven by the AFM correlation. The K_4CdCl_6 type $\text{Ca}_3\text{LiOsO}_6$ is another Os^{5+} oxide with the $5d^3$ electronic configuration, in which the t_{2g} orbitals are half-filled with $S = 3/2$. Similarly, the SOC is weak in this case, and it is not surprising that the calculation with LDA+SOC can not split the Os 5d t_{2g} bands into two manifolds[9]. However, comparing with $\text{Cd}_2\text{Os}_2\text{O}_7$, half Os atoms are replaced by Li atoms in $\text{Ca}_3\text{LiOsO}_6$. The nearest-neighbor Os atoms are rather distant, and the magnetic interaction is expected to be rather weak, regardless of the structural anisotropy. Therefore, the magnetic frustration is al-

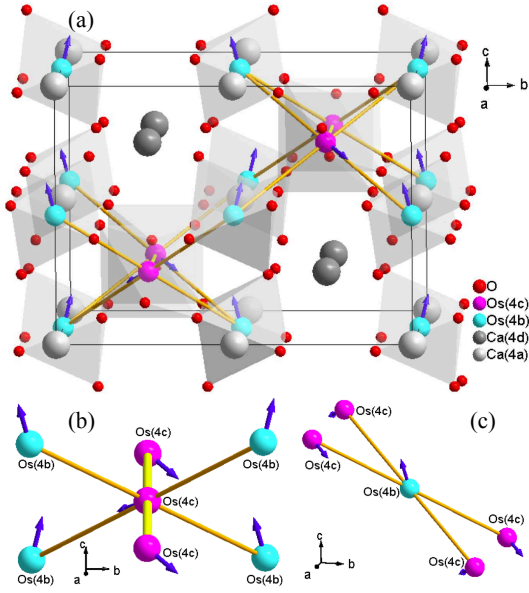


FIG. 1: (a) The crystal structure of $\text{Ca}_2\text{Os}_2\text{O}_7$, with the 4a-site Ca^{2+} on $(0, 0, 0)$, the 4d-site Ca^{2+} on $(1/4, 1/4, 3/4)$, the 4c-site Os^{5+} on $(1/4, 1/4, 1/4)$ and the 4b-site Os^{5+} on $(0, 0, 1/2)$ in the crystal. (b) Coordination environments of $\text{Os}(4c)$ in $\text{Ca}_2\text{Os}_2\text{O}_7$. (c) Coordination environments of $\text{Os}(4b)$ in $\text{Ca}_2\text{Os}_2\text{O}_7$. A dark blue arrow represents a spin director of Os ion. The orange bonds connect the nearest neighboring $\text{Os}(4b)$ and $\text{Os}(4c)$ ions. The yellow bonds connect the nearest neighboring $\text{Os}(4c)$ and $\text{Os}(4c)$ ions.

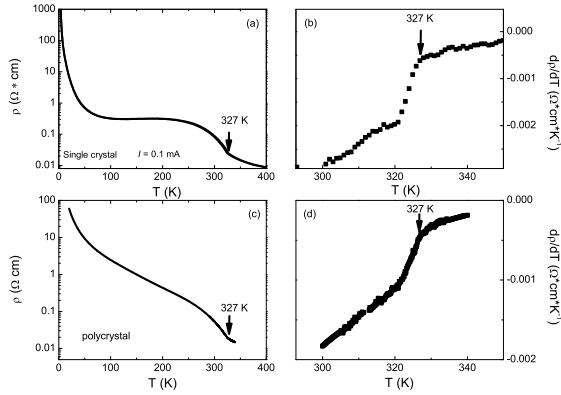


FIG. 2: (a), (b), (c) and (d) The temperature dependence of resistivity (ρ) and $d\rho/dT$ of $\text{Ca}_2\text{Os}_2\text{O}_7$ single crystal and polycrystalline sample respectively.

most quenched. Band structure calculation shows that the bandwidth of t_{2g} bands is narrower than for other typical Os oxides. The smaller bandwidth is a direct consequence of the local structure around Os atoms[9]. The narrow t_{2g} bands suggest that correlation effects are important for this compound, although the Coulomb interaction is expected to be weak due to the nature of the 5d orbital. Shi et al claim that $\text{Ca}_3\text{LiOsO}_6$ can be considered as a 5d Mott insulator, which stabilized within a collinear AFM(anti-parallel) phase[9].

$\text{Ca}_2\text{Os}_2\text{O}_7$ is another Os^{5+} oxide with the 5d³ electronic configuration but adopts the Weberite structure[8] (see Fig. 1). In this structure, Ca cations have two different coordinations (4a and 4d) with eight oxygen ions. Each Os^{5+} is octahedrally coordinated by six nearest oxygen atoms. There are two different Os cation environments. One is $\text{Os}(4b)$ site, which coordinates with four un-frustrated nearest neighboring $\text{Os}(4c)$ cations. The other one is $\text{Os}(4c)$ site, which has six nearest neighboring Os cations. Beside four un-frustrated $\text{Os}(4b)$ cations, it also coordinated by two frustrated $\text{Os}(4c)$ cations. So we name $\text{Ca}_2\text{Os}_2\text{O}_7$ as the half-frustrated system. The frustration effect would lead to a non-collinear magnetic interaction[12]. Up to now, only the temperature dependences of resistivity and crystal structure on polycrystal were reported. Similar to $\text{Cd}_2\text{Os}_2\text{O}_7$, $\text{Ca}_2\text{Os}_2\text{O}_7$ also has an insulating ground state[8] and shows a metal-insulator-like transition. However, its magnetic properties, electronic structure and the origin of the M-I transition are not studied yet. In this work, we present investigations on $\text{Ca}_2\text{Os}_2\text{O}_7$ by the resistance, specific heat, magnetization and optical reflectance measurements. The resistivity reproduces the behavior reported in ref.[8], which also shows an insulating state at low temperature. Zero electronic specific heat is observed, implying a full gap at the low temperature. In the mean time, a spectral weight transferring from low frequency to high frequency in optical conductivity is observed with decreasing temperature, conforming the gap opening in the insulating state. High temperature magnetization study indicates that the system is stabilized in high spin state with $S = 3/2$. To explain the experimental observations, the first principles calculations are performed. We find that the AFM correlation with intermediate Coulomb repulsion U play important roles during $\text{Os}(4b)$ bands splitting. But for $\text{Os}(4c)$ bands, the non-collinear magnetic interaction is the another necessary factor.

II. EXPERIMENTS

High density polycrystal and small single crystal samples were prepared in a high-pressure apparatus. The stoichiometric mixtures of CaO , OsO_2 (Os -84.0%, Alfa Aesar) and KClO_4 were placed into a platinum capsule, and sintered in a belt-type high-pressure apparatus at 1300 °C for 1 hour under a pressure of 3 GPa. We washed the polycrystal to remove the KCl flux. The powder samples were pressed again at 6 GPa to get the condensed pellet, which were used for measuring the specific heat, resistivity, and optical reflectance data. The single crystal grew under a stable pressure of 3 GPa during heating at 1500 °C for 2 hours (KCl as flux provided by KClO_4), then was slowly cooled down to 1300 °C for 3 hours. Thereafter, the capsule was quenched to ambient pressure and temperature. The samples were washed by water for several times and we could find some single crystals. Typically,

TABLE I: The parameters of the crystal structure and main interatomic distances at room temperature; group space: $Imma$; cell parameters: $a = 7.2165\text{\AA}$, $b = 10.1385\text{\AA}$, $c = 7.3844\text{\AA}$; Ca(4a) on (0, 0, 0), Ca(4d) on (1/4, 1/4, 3/4), Os(4c) on (1/4, 1/4, 1/4), Os(4b) on (0, 0, 1/2), O1 on (0, 1/4, 0.1625), O2 on (0, 0.4038, 0.7279); O3 on (0.2054, 0.3834, 0.4356).

$Ca(4a) - O2$	2.2335Å
$Ca(4d) - O2$	2.3902Å
$Os(4c) - O1$	1.9163 Å
$Os(4b) - O2$	1.9451 Å
$Os(4b) - Os(4c)$	3.6176 Å
$Os(4c) - Os(4c)$	3.6082 Å

the crystals have square shape of surface with edge length about 0.2 mm. The largest single crystal has the edge length about 0.5 mm. X-ray diffraction measurement at room temperature indicates that the samples are of single phase with Webrite structure. The crystal structure and main interatomic distances are collected in table. I, which are very close to the previous report[8]. The dc resistivity ($\rho(T)$) and the specific heat(C_p) measurements were carried out on a Quantum Design physical property measurement system (PPMS). The magnetization was measured on a Quantum Design (SQUID) VSM. The optical reflectance $R(w)$ of $Ca_2Os_2O_7$ was measured from 30 cm^{-1} to 25000 cm^{-1} at different temperatures on a Fourier transform spectrometer (Bruker 80v). Standard Kramers-Kronig transformations were employed to derive the frequency-dependent optical conductivity. For low frequency extrapolations, we use Hagen-Rubens relation for the measurements above 300 K and constant values for reflectance data below 200 K. In fact, it is found that the different low frequency extrapolations do not affect the conductivity spectra in the measured frequency region. In the high energy side, the measured reflectance curve is extrapolated constantly to 100000 cm^{-1} , above which a well-known function of ω^{-4} is used.

The electronic structures of $Ca_2Os_2O_7$ are studied by first principle calculations using BSTATE and VASP packages. Both of them are based on plane-wave method with pseudopotential scheme, and give consistent results. The generalized gradient approximation (GGA) of PBE-type [13] and its variant GGA+U method are used for the exchange-correlation energy. Nonmagnetic (NM), collinear anti-ferromagnetic (AFM) and non-collinear magnetic states are considered in present study. All calculations are performed with the experimental lattice parameters and internal coordinates. Spin-orbital coupling (SOC) is considered in all calculations. However, as identified in other Os^{5+} compounds such as $Cd_2Os_2O_7$ [14] and Ca_3LiOsO_6 [9], SOC plays very weak roles on the NM electronic structures and collinear magnetism.

The temperature dependent dc resistivities ($\rho(T)$) for both single crystal and polycrystalline samples are shown in Fig. 2. They show similar temperature dependence.

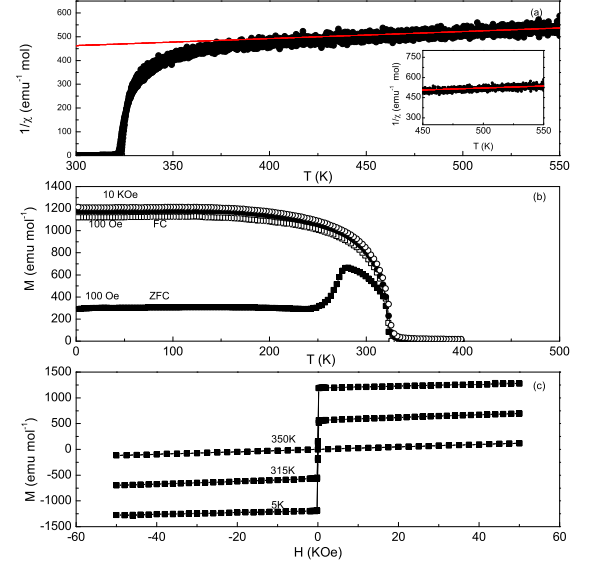


FIG. 3: (Color online) (a) The inverse susceptibility as a function of temperature of the polycrystal $Ca_2Os_2O_7$ between 300 K and 550 K in the field of 10 KOe. The inset is $1/\chi(T)$ from 450 K to 550 K with a red line representing the Curie-Weiss law fitting. (b) The temperature dependencies of the magnetization of $Ca_2Os_2O_7$ single crystal in the magnetic fields of 100 Oe (squares) and 10 KOe (circles) after zero field cooling (ZFC) (solid ones) and field cooling (FC) (hollow ones) respectively. (c) The field dependencies of the magnetization of $Ca_2Os_2O_7$ measured at 350 K, 315 K and 5 K respectively.

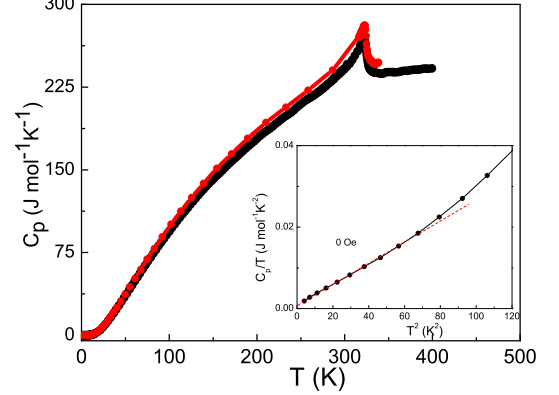


FIG. 4: The temperature dependencies of specific heat of ten $Ca_2Os_2O_7$ single crystals (black ■) and polycrystal (red ●). The inset is the enlargement of the low temperature part of C_p/T vs T^2 .

A spinodal feature could be found in $\rho(T)$. The spinodals of the two samples appear at the same temperature (Fig. 2 (a) and (c)). The resistivity at 300 K is ten times higher than the value for $Cd_2Os_2O_7$ [11] but one percent of the value for Ca_3LiOsO_6 [9]. We calculate their $d\rho/dT$ (Fig. 2 (b) and (d)) to determine the phase transition temperature. The sharp drop of $d\rho/dT$ begins at 327 K for both samples. $d\rho/dT$ of the single crystal changes more pronouncedly than that of polycrystal. Both the XRD result

and the $\rho(T)$ imply the high quality of our samples and that the polycrystalline sample is very close to the single crystal.

The magnetic properties of $\text{Ca}_2\text{Os}_2\text{O}_7$ under magnetic fields are shown in Fig. 3 (a) (b) and (c). Figure 3 (a) is the inverse susceptibility ($1/\chi(T)$) from 300 K to 550 K. An abrupt change occurs at the same critical temperature with the resistivity anomaly. The data between 320 K and 400 K deviate from the linear-T dependence. When temperature is higher than 400 K, $1/\chi$ shows a good linear relation with T, suggesting a paramagnetic Curie-Weiss behavior, $\chi = N\mu_0\mu_J^2/3k_B(T - \theta)$, from which we can estimate the system's intrinsic magnetic moment, in terms of $C = N\mu_0\mu_J^2/3k_B$. Here θ is the Weiss temperature; N is the Avogadro's constant; k_B is the Boltzmann constant; $\mu_J = g\sqrt{S(S+1)}\mu_B$ (Lande factor $g=2$) is the intrinsic magnetic moment. By fitting the data from 450 K to 550 K (shown in the inset of Fig. 3(a)), the intrinsic magnetic moment per Os ion is determined to be $2.59\mu_B$. This value is about 67% of the expected moment ($3.87\mu_B/\text{Os}$) for $S=3/2$ configuration, indicating that the spins of Os 5d electrons are in the $S=3/2$ high spin state. θ is -1263 K, suggesting a strong antiferromagnetic interaction.

Figure 3 (b) shows the temperature dependences of the magnetization $M(T)$ measured with 100 Oe and 10 kOe field respectively. Each measurement was performed under zero field cooling (ZFC) and field cooling (FC) respectively. Steep change of $M(T)$ at 327 K could be observed in all the curves, suggesting the establishment of a long range magnetic ordering at $T = 327$ K. The ZFC data measured under 10 kOe is the same with the FC data. Since high magnetic field may make the spins polarized, the intrinsic magnetic properties of the system may not be completely revealed. Therefore, a small field 100 Oe ZFC is used, which may reflect more intrinsic information of the system. Looking at the ZFC $M(T)$ curve under 100 Oe, we can see that the magnetization keeps a small constant value until 250 K, and increases to the maximum at about 280 K. It drops abruptly at about 327 K and decreases weakly with T increasing further. Such a ZFC $M(T)$ is the typical behavior of the ferrimagnetic ordering or the canted AFM ordering with small net moments. From the data measured at 5 K shown in Fig. 3(c), we get the magnetization to be $1200 \text{ emu mol}^{-1}$ at the largest field 50 kOe, equaling to $0.107\mu_B$ per Os. The net moment is only 3.6% of the expected moment for $S=3/2$.

In Fig. 4, we plot C_p vs T for single crystal (represented by black squares) and polycrystal (represented by the red circles). The experimental curves of polycrystal and single crystal have the same shape and show phase transition at the same temperature. For both samples, the specific-heat anomaly starts at about 327 K and gets to a maximum at 323 K. It corresponds to the transition observed in the resistance and magnetic measurements. The shape of the specific-heat anomaly is λ -like, indicating that the transition is a second-order phase transition.

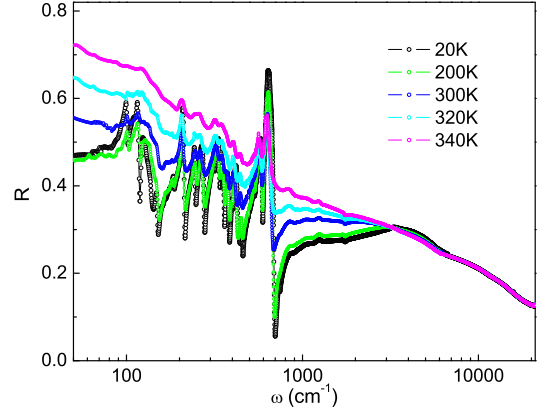


FIG. 5: (Color online) The frequency dependence of reflectivity $R(\omega)$ at 340 K, 320 K, 300 K, 200 K and 20 K in the frequency region from 50 cm^{-1} to $22,000 \text{ cm}^{-1}$, respectively.

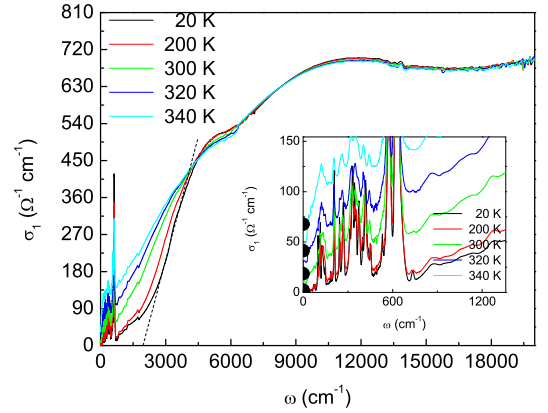


FIG. 6: (Color online) Frequency dependence of the optical conductivity $\sigma_1(\omega)$ at different temperatures. The dashed line shows the steepest dropping of the conductivity and crossing the ω -axis which is defined as the direct gap 2Δ . The inset is the enlarged scale of $\sigma_1(\omega)$ in which the black points are the dc resistivities at the relative temperatures.

This behavior is consistent with that no crystal structure phase transition was observed in the variable temperature crystal structure analysis in ref. [8]. The inset of Fig. 4 shows the low-temperature part of C_p/T vs T^2 (solid line) and the fitting result (dashed line) using formula $C_p(T)/T = \beta T^2 + \gamma$. One can see that the function could well fit the data at $T < 7$ K. The T^3 term in $C_p(T)$ could be attributed to either phonon or/and magnon contributions. The linear term is the contribution from the electrons. We found that the low-temperature C_p/T approach a small value ($< 1.4 \text{ mJ mol}^{-1} \text{ K}^{-2}$) in the limit of $T \rightarrow 0$, indicating the vanishing of the density of states. It implies that the system is fully gapped.

To understand the phase transition, we have to know the electronic structure of $\text{Ca}_2\text{Os}_2\text{O}_7$. Optical spectroscopy is a powerful tool to probe the electronic structure and charge dynamics. We measured the reflectivity spectra from 30 cm^{-1} to 22000 cm^{-1} at various tempera-

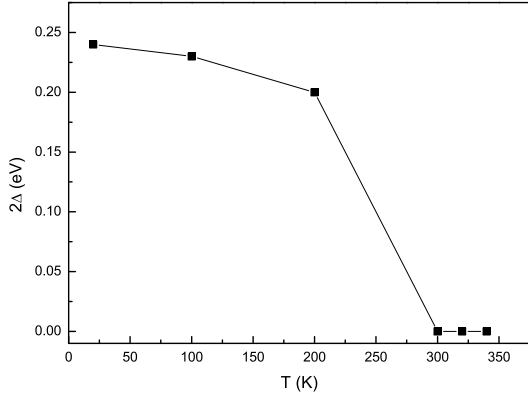


FIG. 7: (Color online) The development of the direct gap with temperature.

tures and plotted them in Fig. 5. Figure 6 is a collection of the real part of the optical conductivity $\sigma_1(\omega)$ between 20 K and 340 K. The black points in the inset are the dc conductivity from Fig. 2 (c), which match with the lowest frequency optical conductivity very well. We can see that there are a lot of phonon responses in the optical conductivity spectra. Even at 340 K, the conductivity decreases with decreasing ω . Although a Drude-like response is not visible, the value of $\sigma_1(\omega)$ at the lowest frequency does not vanish. The data indicate that the compound may have a few itinerant carriers at high temperature, which contribute to a small Drude component. A quantitative analysis will be presented below. With decreasing T, the phonon peaks become more pronounced. We found that some modes, for example 577 cm^{-1} and 641.5 cm^{-1} , weakly harden when $T < 320 \text{ K}$, indicating some bonds weakly shrinking in the crystal structure[8].

The conductivity spectra display two inter-band transition peaks at about 5000 cm^{-1} (about 0.6 eV) and 11000 cm^{-1} (about 1.3 eV). A full gap could be clearly observed below 200 K. This is also consistent with the zero electron specific heat in Fig. 4. With the temperature decreasing, the spectral weight transfers from low frequency to high frequency and a direct gap opens gradually. To determine the energy gap at 20 K, we draw a dashed line to fit the steepest part of $\sigma_1(\omega)$ in Fig. 6. Extending the line to the ω -axis, the crossing appears at $2\Delta \approx 2000 \text{ cm}^{-1}$, which corresponds to the direct gap. Using the same way, we determine the gap at different temperatures and collect them in Fig. 7, showing how the direct gap develops with the temperature varying. A relatively large gap opens at the same temperature as that shown in the magnetization and specific heat measurements. Consistent with a strongly correlated material, the gap opens at a temperature much lower than the size $k_B T_{AFM} \ll 2\Delta$.

We noticed that at $T > 300 \text{ K}$, the optical conductivity spectra do not simply follow the Lorentz lineshape in the low frequency region. As described above, an abrupt increasing reflectivity with the frequency decreasing could

TABLE II: The parameters of function(1) at 340 K and 20 K

$T(K)$	function	$\omega_0(\text{cm}^{-1})$	$\omega_p(\text{cm}^{-1})$	$\gamma(\text{cm}^{-1})$
340K	Drude	0	4400	2600
	Lorentz1	4500	12600	9300
	Lorentz2	12300	22000	14900
20K	Drude	0	0	0
	Lorentz1	4500	13600	9300
	Lorentz2	12300	22000	14900

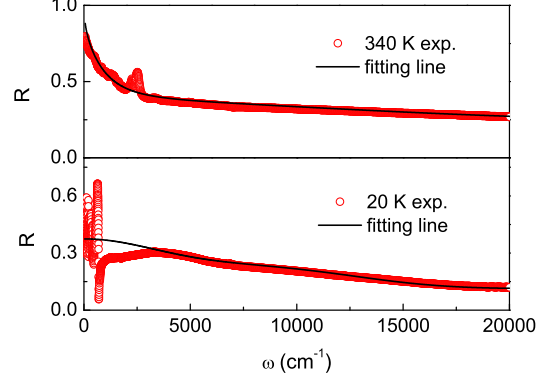


FIG. 8: (Color online) Fitting the frequency dependence of reflectivity $R(\omega)$ at 340 K and 20 K respectively. The circles represent the raw data and the solid line is the fitting line using the Drude-Lorentz model.

be clearly observed in the far infrared region. When the gap completely opens, the reflectivity is almost frequency independent as shown in Fig. 5. We used the Drude - Lorentz model to fit the reflectivity at 340 K and 20 K, respectively:

$$\varepsilon(\omega) = \varepsilon_\infty - \frac{\omega_p^2}{\omega^2 + i\gamma\omega} + \sum_j^N \frac{S_j^2}{\omega_{0j}^2 - \omega^2 - i\gamma_j\omega}. \quad (1)$$

where ε_∞ is the high-frequency dielectric constant; the middle and last terms are the Drude and Lorentz components, respectively. The fitting results are shown in Fig. 8. A Drude term and two Lorentz terms were used to fit the reflectivity at 340 K and 20 K respectively, which match the raw data very well. The parameters are listed in Table II. This analysis leads to $\omega_p = 4383 \text{ cm}^{-1}$ and the scattering rate $1/\tau = 2572 \text{ cm}^{-1}$ for the Drude component at 340 K. At 20 K, the Drude component becomes vanishing; thus, two Lorentz terms could roughly reproduce the reflectivity as shown in the down-part of Fig. 8. The fitting results confirm that there should be some short-life time itinerant carriers in the system at 340 K, which is completely gaped at 20 K.

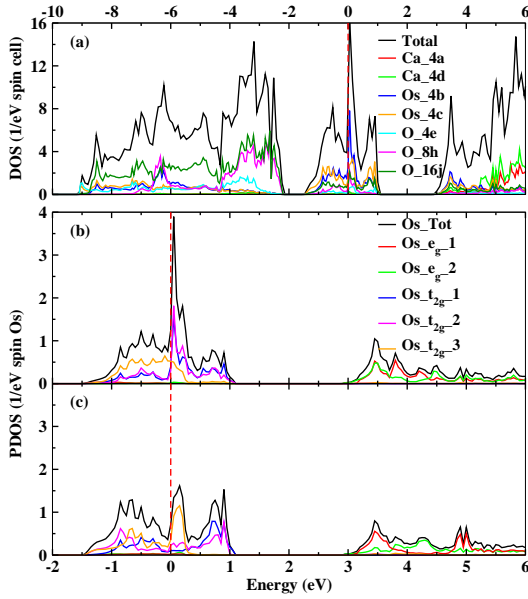


FIG. 9: (Color online) The calculated electronic properties of NM states without SOC. (a) is the DOS and PDOS in a primitive cell. (b) and (c) are the PDOS on 5d orbitals of Os(4b) and Os(4c). Fermi level E_F is defined at 0, denoting as the vertical red dash line.

III. CALCULATION AND DISCUSSIONS

The electronic structures of $\text{Ca}_2\text{Os}_2\text{O}_7$ are calculated using density functional method. Because SOC has little influence on the Os^{5+} compounds, we only show the total and projected densities of states (DOS and PDOS) for the nonmagnetic calculation without SOC in Fig. 9. From Fig. 9 (a) we can see that the t_{2g} and e_g manifolds are clearly separated from each other due to the octahedral crystal field effect, and from the O 2p bands by clean gaps. As a result, the t_{2g} manifolds mostly occupy from -1.5 eV to 1.1 eV for both Os 4b and 4c sites as shown in Fig.9 (b) and (c), well separated from the unoccupied e_g manifolds which are strongly hybridized with O 2p orbitals and localized between 3 and 5 eV. We can see that the t_{2g} manifolds are half filled and contain 12 bands, confirming that there are 2 Os(4b) and 2 Os(4c) ions per unit cell, and each Os ion's valence is exactly +5. The t_{2g} band widths for both Os(4b) and Os(4c) are approximately 2.6 eV, very similar to 2.85 eV of $\text{Cd}_2\text{Os}_2\text{O}_7$ [14], but much wider than $\text{Ca}_3\text{LiOsO}_6$'s 1.2 eV [9]. This means that: 1) the 4b and 4c sites have the similar local conditions around Os ions from the nonmagnetic view; 2) the on-site Coulomb interaction itself could not be responsible for $\text{Ca}_2\text{Os}_2\text{O}_7$'s insulating ground state; 3) the distance between the nearest Os neighbors $d_{\text{Os-Os}}$ plays an important role for their t_{2g} band width in the Os^{5+} compounds. For example, the average $d_{\text{Os-Os}}$ of $\text{Ca}_2\text{Os}_2\text{O}_7$ is about 3.605 Å, very close to $\text{Cd}_2\text{Os}_2\text{O}_7$'s 3.592 Å, but much smaller than that in $\text{Ca}_3\text{LiOsO}_6$ (about 5.648 Å). So that the former two

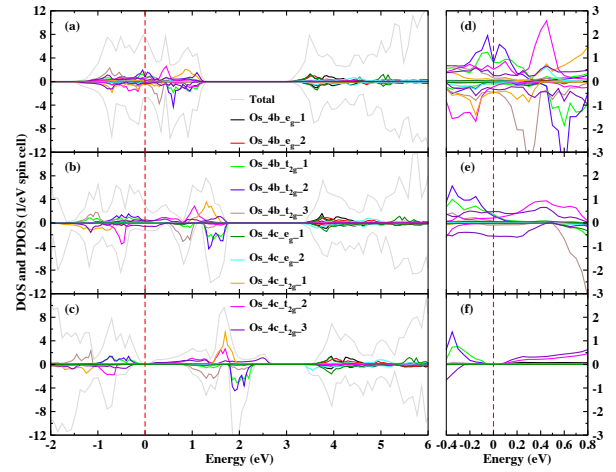


FIG. 10: (Color online) The calculated electronic properties of the collinear AFM states without SOC by GGA (+ U) method. (a), (b) and (c) are the results calculated by U = 0 (GGA), 2 and 4 eV respectively. The positive and negative show partial DOS for up and down spins, respectively. Vertical red dash denotes the Fermi level E_F . (d), (e) and (f) are the enlargements of the Fermi level region of (a), (b) and (c) respectively.

have the similar t_{2g} band widths, while the latter one is much narrower than them.

It should be noted that the high value of DOS at E_F ($N(E_F) = 13.203 \text{ eV}^{-1}$ per cell) obtained in $\text{Ca}_2\text{Os}_2\text{O}_7$ would lead to strong magnetic instability in this material. In order to investigate the possible magnetic order and the insulating ground state, we have performed GGA+U calculation for a collinear AFM state, where the moments on 4b and 4c sites are assumed to be opposite. The results are shown in Fig. 10, from which we can see that the $N(E_F)$ of GGA is reduced to 7.646 eV^{-1} per cell when collinear AFM is considered, and the total energy is about 155 meV/cell lower than NM state. With U increasing, the up and down spin orbitals on one site will further split, leading to the reduction of $N(E_F)$. An insulating state is reached at U = 4 eV. Such a large U is obviously unreasonable for a 5d metal oxide. However, if we carefully examine the process of gap opening, some useful clues become clear. One important character of Fig.10 is that the collinear AFM correlation can obviously narrow the t_{2g} bands on 4b-sites, while has weak effect on 4c-sites. Taking the majority channel (up spin for 4b and down spin for 4c) calculated by GGA as an example, the band width of 4b becomes 2 eV ranging from -1.5 to 0.5 eV, but the band width of 4c remains 2.5 eV localized between -1.5 and 1.0 eV. Thus, when the Coulomb repulsion U increases to 2 eV, a full gap opens between up and down spin channels of 4b-sites as shown in Fig.10 (b), while the 4c-sites remains metallic until the unreasonable U = 4 eV is used. These different behaviors of the electronic structures between 4b and 4c remind us their different conditions of the nearest neighbor Os ions. In the view of the nearest Os-Os spin interaction,

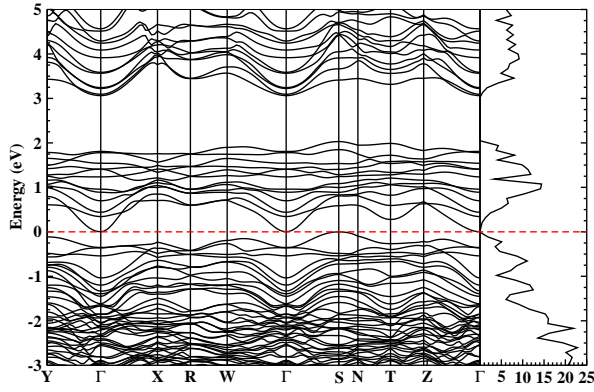


FIG. 11: (Color online) The calculated electronic properties of the non-collinear magnetic states by GGA + U method with SOC and $U = 2.5$ eV. The left panel is the band structure, where the high symmetry points are defined as Y(0.5,-0.5,0.5), Γ (0,0,0), X(-0.377,0.377,0.377), R(0,0,0.5), W(0.25,0.25,0.25), S(0,0.5,0.5), N(0.255,0.378,-0.005), T(0.5,0,0) and Z(0.383,0.383,-0.383), and the right panel is the corresponding DOS with unit $1/(\text{eV cell})$. Red dash denotes the Fermi level E_F .

one 4b-site spin is coordinated by four opposite spins on 4c-site. However, for the 4c-site, besides the AFM interaction with four opposite spins on 4b-site, it is frustrated with other two 4c-site spins, *i.e.* the spins between 4c-sites have ferromagnetic interaction with each other. In this circumstance, we think that the electronic properties of 4b-site Os ions in $\text{Ca}_2\text{Os}_2\text{O}_7$ is very similar to NaOsO_3 [15], where the gap opening is duo to the dual effect of AFM correlation and Coulomb repulsion. On the other hand, the physics on 4c-site is more or less like what happened in $\text{Cd}_2\text{Os}_2\text{O}_7$, where magnetic frustration play an important role. Considering our resistance and optical measurements that $\text{Ca}_2\text{Os}_2\text{O}_7$ undergoes a wide temperature region to transform into the real insulating state, we identify that the electronic structures on 4c-site experience a Slater transition.

In order to find the real magnetic states, magnetic frustration must be correctly dealt with. Thus we perform GGA + U method with SOC to calculate the non-

collinear magnetic states of $\text{Ca}_2\text{Os}_2\text{O}_7$, and obtain an insulating solution with a plausible Hubbard U (2.5 eV). The results are shown in Fig. 11, from which we find that a direct gap about 0.35 eV is opened, very close to the data (0.24 eV) deduced by optical measurements. Moreover, based on the non-collinear magnetic DOS, the inter-band transition at 5000 cm^{-1} (about 0.6 eV) and 12000 cm^{-1} (about 1.5 eV) in $\sigma_1(\omega)$ correspond to the hopping from -0.2 eV to 0.6 eV and -0.6 eV to 1.0 eV very well. Notes that the Os 5d t_{2g} orbitals are hybridized with O 2p orbitals, and the moments (spin) are non-collinear now, so that the hopping could happen. The calculated moment direction for each Os is shown as arrow in Fig.1. We think that the measured net magnetic moments at low temperature are derived from the non-collinear arrangement on Os.

IV. CONCLUSION

We report our specific heat, magnetization and the optical reflectance investigations on $\text{Ca}_2\text{Os}_2\text{O}_7$. The phase transition is revealed by all the experiments. An energy gap is observed developing with decreasing temperature in the optical measurements. Along with the gap opening, a net ZFC magnetic moment appears and the spectral weight in low frequency region is transferred to higher frequency region. We performed the first principle calculations and found that the anti-ferromagnetic (AFM) correlation with intermediate Coulomb repulsion U could effectively split Os(4b) t_{2g} bands and push them away from Fermi level (E_F), while a non-collinear magnetic interaction is needed to push the Os(4c) bands away from E_F , which could be induced by Os(4c)-Os(4c) frustration.

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